Atomistic Simulations of Filled Polymers: PDMS / Silica Systems

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Filled polymers are an important class of materials serving diverse applications. Automobile tires contain a mixture of carbon black and butyl rubber, and ordinary silicone calking compound is a mixture of polydimethyl-siloxane (PDMS) and silica. PDMS/silica mixtures are also used extensively in nuclear weapons to provide cushioning and mechanical support. A chemisty-based strength model is essential in order to understand how these materials degrade with time, and a knowledge of the fundamental chemical processes that produce and affect material strength is a vital prerequisite to developing such a model.

Figure 1.

It is well known from experiment [1] that the strength of PDMS increases by a factor of ~40 if small (~0.1 - 0.5 mm) silica particles are added. Unlike conventional rubbers, cross linking alone does not produce significant strength in PDMS. Therefore, we conclude, that it is the interaction (bonding) of the PDMS polymers with the surfaces of the silica particles that produces strength. We have performed atomistic simulations on PDMS polymer chains and their interaction with a hydroxylated silica surface to determine fundamental forces which affect or contribute to strength.

A knowledge of the fundamental chemical processes that produce and affect material strength is necessary to understand how the material ages.

Two types of simulations were performed: detaching a short strand of PDMS from a hydroxylated silica surface (Figure 1), and stretching, or uncoiling a single strand of PDMS by pulling on the ends. The procedure for these calculations was as follows: After the ene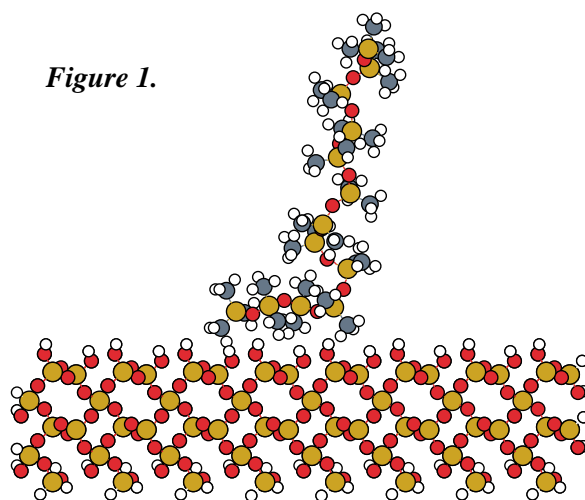rgy of the system was minimized, the end Si atom of the PDMS chain was translated vertically by 0.5 Å and a new minimum conformation was calculated. For the chain stretching case, both end atoms were fixed, and, for the detachment case, the Si substrate was fixed as well as the end atom. At the end of a series of calculations, we plotted the total system energy vs. the distance the end atom was moved. The data for the detachment case is shown in Figure 2 where it is clear that the energy is approximately linear with respect to distance. From this, we conclude that the force (dE/dy) required to detach a single strand of PDMS from a hydroxylated silica surface is a constant (~8×10^{-6} dynes). Surprisingly, the force required to stretch a single strand of PDMS from a minimized state is also a constant (~3×10^{-6} dynes). Due to computational limitations, it was not possible to include a representative sample of the surrounding PDMS material. However, including two neighboring PDMS strands did not affect the force required to stretch a single PDMS chain. Integration times were probably far too short for entropic effects to manifest themselves, however, experiments [2] suggest that the entropic contribution to the strength of PDMS/silica is less than that due to changes in internal energy.

From these two forces, we can make a prediction about how bulk PDMS / silica systems should behave under

extension. Initially, the material should exhibit a yield stress due to the finite force required to stretch a PDMS chain. As the PDMS strands become nearly straight, further extension causes them to detach from the surface of the silica particles. Since this force is greater than that required to stretch a chain, the required stress should increase. Ultimately, for a stress sufficient to detach all the PDMS strands connecting silica particles, the material should fail (the tensile strength). This predicted ratio of tensile strength to yield stress, ~7, and the overall stress/strain behavior is consistent with published experiments1.

We are in the process of constructing a numerical mesoscale model as an explicit node/polymer chain assembly, where the properties of the polymer chains and their interactions with the silica surfaces are determined from atomistic simulations described above. Such a model will capture the essential processes that produce and affect strength. It will also provide a robust platform for incorporating additional physics and chemistry and a be a valuable tool for simulating experiments on filled polymers.
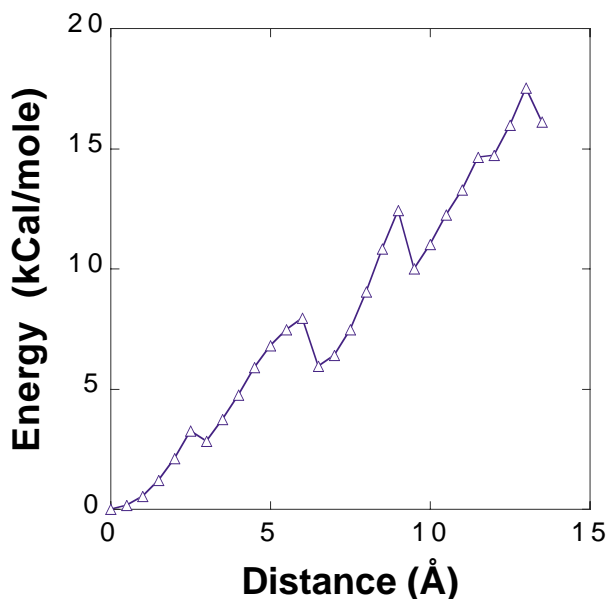

Figure 2.

[1] B. B. Boonstra et al., *Rub. Chem. and. Tech.* **48**, 559 (1975).

[2] A. V. Galanti and L. H. Sperling, *Polymer Engineering and Science* **10**, 177 (1970).